at High Pressures and Temperatures

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Self-propagating synthesis can be an economical method for the preparation of advanced materials if the basic problem of porosity is overcome. The application of pressure during a self-propagating combustion reaction (HPCS) results in dense ceramic materials. Starting from elemental powders, dense compacts of ceramics and ceramic composite materials (TiB_2, TiB_2-TiC, TiB_2-TiN, Ti_3SiC_2, NiAl-TiB_2 etc.) were prepared by conducting the simultaneous synthesis and sintering at high pressures and temperatures. [**Keywords**: ceramics, synthesis, sintering, composites, pressure]

1. Introduction

There has been a growing demand for new materials for structural components related to nuclear, aerospace and energy efficient propulsion applications. Ceramic materials such as refractory carbides and borides which have high melting point, superior mechanical properties and greater chemical stability compared to metals and alloys have received attention. High melting temperatures and elastic moduli indicate the strong covalent nature of bonding in these solids. The covalent bonding which provides these superior properties also tends to retard the solid state sintering due to the slow bulk diffusion. Attempts have been made to consolidate ceramic powders into dense solid bodies by reaction sintering, pressureless sintering and hot pressing with/without sintering aids. In most cases, the consolidation requires temperatures ~2400K and long durations (over 3600s). This results in exaggerated grain growth and the compacts thus obtained have inferior mechanical properties. The use of additives brings down the sintering temperature but, the resulting compacts have inferior mechanical properties at high temperature because of the formation of low melting phases at the grain boundaries.

Self-propagating synthesis (SHS), also known as combustion synthesis, is a process that involves a reaction, which is sufficiently exothermic to sustain itself. This has led to a low cost, energetically efficient method for the development of advanced materials [1-5]. One of the major drawbacks in the SHS of ceramic materials is the porous nature of the products, which require a densification step for any practical application. The ideal production process would be to combine the synthesis and densification step into a one-step process (HPCS) [6,7]. Simultaneous synthesis and sintering under pressure has the advantage that dense ceramic materials can be produced without any sintering aids.

Titanium di-boride and titanium carbide are important materials for light armour, cutting tool, wear parts and high temperature applications, because of their high melting points and hardness, and low density. Ti_3SiC_2 is a machinable ceramic with low hardness and good oxidation resistance, and is a potential material for aerospace applications. Intermetallic matrix composites are a new class of engineering materials for high temperature applications in oxidizing and aggressive environments. This paper will discuss the simultaneous synthesis and sintering of monolithic and composite ceramic materials using the self-combustion synthesis under high pressures and temperatures. The simultaneous combustion mode, wherein the whole compact is heated, was used in this investigation. The results on the synthesis and sintering of TiB_2, TiB_2-TiC, NiAl-TiB_2, TiB_2-TiN and Ti_3SiC_2 are presented.

2. Experimental

The details of raw materials used are listed in Table 1. The following reactions were used to synthesize monolithic and composite ceramic materials:

$Ti + 2B \rightarrow TiB_2$

$2Ti + 2B + C \rightarrow TiB_2 + TiC$

$TiB_2 + Ni + Al \rightarrow TiB_2 + NiAl$

$3Ti + SiC + C \rightarrow Ti_3SiC_2$

$3Ti + 2BN \rightarrow TiB_2 + 2TiN$

Table 1. Characteristics of the starting powders

Powder	Purity (%)	Particle size(μm)	Source
Ti	99.5	13	SPMS Powder Met., France
B	99.7	Amorphous	BARC, India
C		Amorphous	Sarabhai Chemicals India
C (graphite)	Ultra high		Ultra Carbon Corp. USA
TiB_2	99.9	10	HC Stark, Germany
TiC	99.5	8.3	Triebacher Chem. Werke, Austria
SiC	99.9	3	SumitomoChemical Co., Japan
Ni	99.9	3.7	INCO, UK
Al	99.3	16.5	ALCOA
B_4C	98	6	SPMS Powder Met., France
BN	99.5	5	Alpha Chemicals, India

The powder mixtures of required compositions were prepared by ball milling in hexane medium for 24hr (Fritsch Pulversette-5 centrifugal mill) and the milled powders were dried in vacuum. The HPCS were conducted at 3 GPa using a cubic anvil apparatus (anvil face 10mm square) capable of generating pressures up to 6.5 GPa and temperatures up to 3300K [8,9]. The reactive hot pressing (RHP) were carried out at 20-40 MPa in a hot press under a flowing argon atmosphere [10]. The

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powder mixtures were cold pressed at 300 MPa into cylindrical compacts (8-13mm diameter and 3-15mm height) and placed in graphite die. The pressure-temperature treated compacts were characterized by density mesurement, x-ray diffraction, and optical and scanning electron microscopy. The hardness and fracture toughness were determined using HSV-20 Shimadzu hardness tester. The fracture toughness was calculated from the equation

$$K_{IC} = 0.0824\ (P/C^{1.5})$$

Where P is the indentation load (N) and C the crack length (μm) [11]. The thermal expansion coefficient was measured in the temperature range 300-1300K using a dilatometer (Harrop Laboratories, Model TDA-H1-PP6) with a heating rate of 10K/min.

3. Results and Discussion

TiB_2 and TiB_2-TiC composites

Various attempts have been made in the past to consolidate TiB_2 and TiC powders [6,7,12-16]. The maximum density achieved with HPCS was 96.5% [6,7]. In the present work, $TiB_2$and TiB_2-TiC composite compacts with 98-99% density are prepared by high pressure self-combustion synthesis (HPCS) from the elemental constituents and high pressure sintering (HPS) of premixed powders. The synthesis and sintering experiments were carried out at 3GPa in the temperature and time ranges 2250-2750 K and 5-300s, respectively. In a typical experiment, the sample was pressurized to 3GPa first and then the temperature was raised by passing current through the graphite tubular heater containing the sample. The desired temperature was reached in ~5s and maintained for 300s. In a few experiments, the heater power was switched off at the end of 5s heating period. The recovered samples were ~3.5mm in diameter and ~4 mm thick.

In the HPSC experiments, a minimum ignition temperature of 2250 K was required to make the reaction self-propagating in both Ti-B and Ti-B-C systems. Below this temperature, the reaction was incomplete, and the compacts contained elemental reactants and substoichiometric product phases. At and above 2250 K, the reaction ran to completion. However, it was necessary to maintain the high temperature for better densification. The microstructures consist of randomly oriented equiaxed grains of TiB_2 and TiC (Fig.1). A high sintering temperature (2750 K) is required to obtain dense TiB_2 compacts (98% density) by HPS. Higher temperatures led to exaggerated grain growth leading to inferior fracture toughness. Compacts with the similar density are obtained at lower sintering temperature (2250 K) when 15 mol% TiC is added to TiB_2. The composite compacts have marginally better fracture toughness than that of monolithic compacts. The compacts prepared by HPCS have superior fracture toughness than those prepared by HPS (Table 2).

TiB_2 - NiAl Composites

Nickel aluminide (NiAl) which has high melting point, low density, high young's modulus and high thermal conductivity is suitable for high temperature applications. The high pressure reaction sintering (HPRS) of NiAl at 2 GPa and 773K is reported to have 98.2% density, good compressive ductility (14.5%) and strength (876 MPa) [17]. The addition of particulate second phase material in an intermetallic matrix would enhance the properties of the matrix. Composites of NiAl

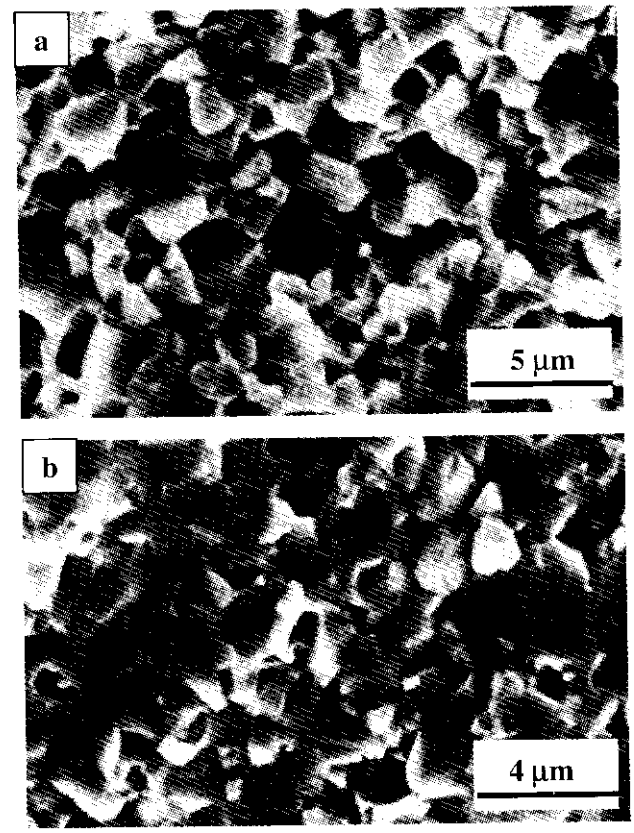

Fig.1. SEM fractographs HPCS (a) TiB_2 and (b) TiB_2-TiC compacts. The microstructures consist of equiaxed grains of TiB_2 and TiC

with Al_2O_3, Y_2O_3 and TiB_2 have been reported [18-22]. In the present work dense TiB_2-NiAl composites with 10, 15 and 30% (volume) NiAl were fabricated from the mixtures of elemental Ni and Al, and TiB_2 powders by HPRS at 3 GPa and 1173 K, and RHP at 20 MPa and 1923 K. The stoichiometric composition of NiAl chosen as the matrix phase has been produced *insitu*. The microstructures of these composites contain equiaxed grains of TiB_2 embedded in the NiAl matrix. Application of pressure is beneficial in obtaining high sintered density at low temperatures, but the associated heat transfer process is the key factor that controls the degree of the reaction. In HPRS, the heat loss by conduction from the reaction zone leads to an incomplete reaction and the compact contained various intermediate phases (Ni_2Al_3, Ni_3Al) (Fig.3). The hardness and fracture toughness values were in the range 10-20 GPa and 3.9-5.7 MPa$\sqrt{m}$ respectively. The RHP compacts contained AlB_2, Ni_2B and $NiTi_2$ phases in addition to those present in the HPRS compacts. The RHP composites were fully dense and had superior hardness (15-22 GPa), but inferior toughness (2.9-3.8 MPa$\sqrt{m}$) compared to those obtained by HPRS. The details of the results are presented elsewhere [23].

TiB_2-TiN, Ti_3SiC_2 Ceramics

Dense TiB_2 -TiC ceramic materials have been produced by the reaction of Ti with B_4C through the formation of an intermediate soft phase at moderate pressures and temperatures [24,25]. The RHP at 7-40 MPa is conducted in two steps:

Table 2. Compositions, synthesis conditions, density, hardness and fracture toughness values.

Sample	Composition (molar ratio)	Temperature (K)	Time (s)	Density (%TD) X (σ)	Hardness (GPa) X (σ)	Fracture toughness K_{IC}(MPa√m) X (σ)
HPS						
	TiB_2	2250	300	94.63 (0.12)	19.2 (1.2)	--
		2500	300	97.11 (0.15)	21.7 (1.5)	2.8 (0.2)
		2750	300	97.95 (0.13)	24.5 (0.8)	3.2(0.1)
	TiB_2 + 15%TiC	2250	300	98.21 (0.09)	22.6 (1.3)	3.5 (0.3)
		2500	300	99.33 (0.11)	23.9 (0.7)	3.9 (0.2)
HPCS						
	Ti+B (1:2)	2250	NH*	97.82 (0.12)	23.6 (1.5)	3.5 (0.4)
		2500	NH	98.04 (0.07)	24.0 (1.2)	3.8 (0.2)
		2750	NH	98.03 (0.16)	23.9 (0.9)	3.6 (0.1)
		2250	300	98.72 (0.13)	24.2 (0.6)	3.9 (0.3)
		2500	300	98.86 (0.17)	24.5 (1.1)	3.8 (0.2)
		2750	300	99.19 (0.06)	24.6 (0.8)	4.5 (0.1)
	Ti+B+C (TiB_2 + 15%TiC)	2250	NH	98.53 (0.08)	22.7 (1.4)	4.3 (0.2)
		2250	300	99.14 (0.10)	23.8 (0.7)	4.2 (0.2)
		2500	300	99.03 (0.05)	23.5 (1.0)	4.6 (0.3)

X is the mean value, σ the standard deviation and %TD the percent theoretical density. * No holding

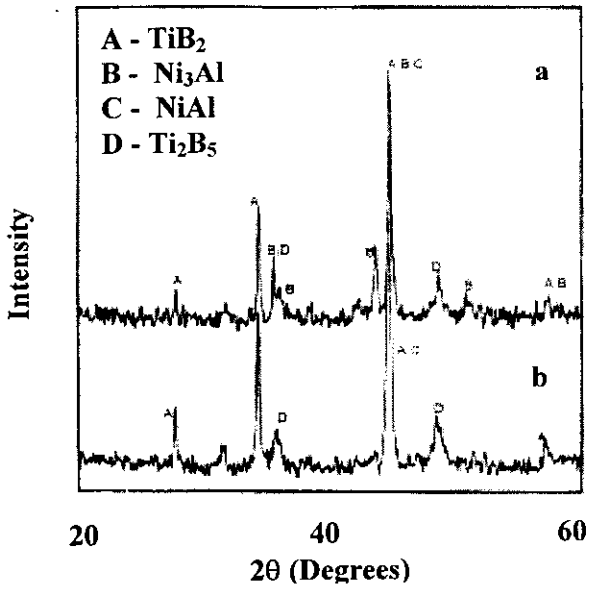

Fig.2. X-ray diffraction patterns of TiB_2-30% NiAl after (a) HPCS and (b) annealing at 1373 K for 7200s.

step I at 1250 K for 2h to form a soft phase followed by step II at 1900 K for 2hr for completion of the reaction and densification in a flowing argon atmosphere. The TiB_2 -TiN composites were produced by the reaction of titanium with boron nitride, with 1% nickel added for better densification. The typical x-ray diffractogram of the TiB_2-TiN composite is shown in Figure 3. The composite was 98% dense, with a hardness of20GPa, fracture toughness of 5.7±0.4MPa√m and a coefficient of thermal expansion $9.1.10^{-6}$ K^{-1}. These are in good agreement with those reported in literature for samples prepared by RHP of TiH_2 and BN [26] and better than those prepared with fine powders [27].

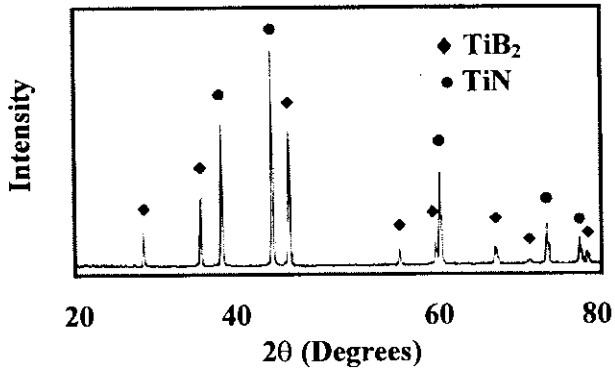

Fig.3. X-ray diffraction pattern of the TiB_2–TiN composite

Ti_3SiC_2

Titanium silicon carbide (Ti_3SiC_2) is a ductile ceramic in the Ti-Si-C system with low hardness and good oxidation resistance. The Ti_3SiC_2 ceramic was produced by hot pressing of the powder mixtures of titanium, silicon carbide and carbon. The x-ray diffraction patterns of the hot-pressed samples

indicated the presence of the ternary Ti_3SiC_2 phase and a small fraction of TiC (Figure 4). The pattern consists of lines corresponding to the Ti_3SiC_2 and TiC phases indicating that the samples were fully equilibriated in the given processing time.

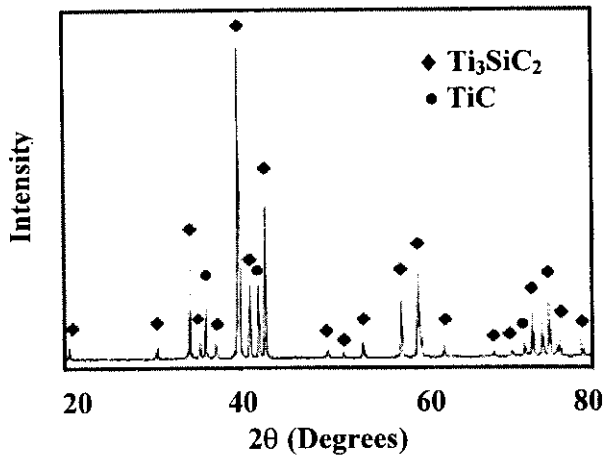

Fig.4. X-ray diffraction pattern of Ti_3SiC_2 ceramic. Lines corresponding to TiC are also seen.

The reason for the presence of TiC may be the incorporation of carbon from the die. No SiC was detected in the XRD patterns. The density values (4.52-4.555 g/cm^3) are close to the theoretical value of 4.53 g/cm^3. Slightly higher values indicate the presence of small amount of TiC_x. The Vickers hardness (H_V) measured on the samples was in the range 370-520. The reported values are 400 for high-purity HIPped material [28], 600 for single crystal [29], 750 in less pure form [30] and 570 in the electron-beam-ignited solid state reaction [31]. The coefficient of thermal expansion at 2000^0 C was 11.7. 10^{-6} /^{0} C. A typical Vickers indentation on the sample at a load of 198N is shown in the Figure 5. The machinability of this ceramic was demonstrated by drilling and threading a hole (Diameter4.7mm, pitch 0.81mm) and cutting an external thread (Diameter 13mm, pitch 1.5mm) using the conventional HSS tools without any coolant.

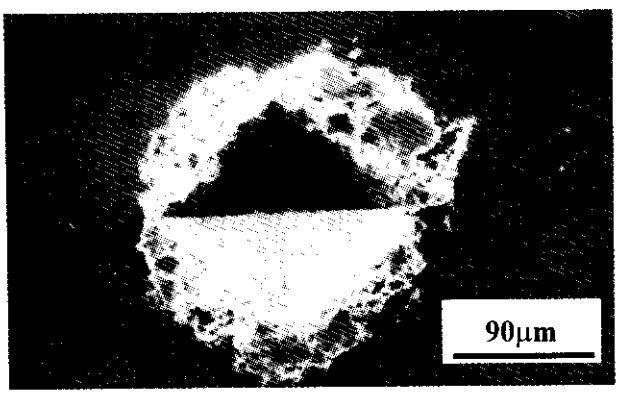

Fig.5. SEM micrograph of an indentation on a Ti_3SiC_2 sample at 198 N load. No cracks are observed from the corners. The surface around the indentation indicates pile up of the material.

4. Conclusions

The fabrication of dense compacts of TiB_2, TiB_2-TiC, TiB_2-TiN ceramic-ceramic composites, TiB_2-NiAl intermetallic - matrix-ceramic composite and Ti_3SiC_2 by the simultaneous synthesis and sintering under pressure has been demonstrated.

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References

[1] A.G.Merzhanov and I.P.Borovinskaya, *Dokl.Chem.* (Eng. Trans.) **204**, 429 (1972)
[2] J.F.Crider, *Ceram. Eng. Sci. Proc.*, **3**, 519 (1982)
[3] Z.A.Munir, *Am.Ceram. Soc. Bull.* **67**, 354 (1988)
[4] J.B.Holt and S.D.Dunmead in *Annual review of materials Science, ed.*R.A.Huggins, J.A.Giordmaine, and J.B.Wachtman Jr., (Annuaal Reviews Inc., CA, 1991), Vol.21, p.305
[5] J.Subrahmanyam and M.Vijayakumar, *J.Mater.Sci.*, **27**, 6249 (1992)
[6] Y.Myamoto, M.Koizumi and O.Yamada, *Commun..Am. Ceram. Soc.*, **67** ,C-224 (1984)
[7] O.Yamada, Y.Myamoto and M.Koizumi, *Common.Am. Ceram.Soc.*, **70**, C-206 (1987)
[8] S.K.Bhaumik, C.Divakar, Murali Mohan and A.K.Singh, *Rev.Sci.Instrum.*, **67**, 3679 (1996)
[9] S.K.Bhaumik, C.Divakar, S.Usha Devi and A.K.Singh, *J.Mat.Res.*, **14**, 906 (1999)
[10] R.Seshadri, B.Dwarakanath Rao, V..Narayanaswamy and L. Rangaraj in *Advances in High Pressure Science & Technology*, ed. A.K.Singh, (Tata McGraw-Hill, New Delhi, 1995), 393
[11] A.G.Evans and T.R.Wilshaw, *Acta Metall.*, **24**, 939 (1976)
[12] H.R.Baungartner and R.A.Steiger,*J.Am.Ceram.Soc.*,**67**,617 (1984)
[13] H.Pastor, in V.I.Malkovich (ed.), *Refractory Borides*, Sprigler Verlag, NY, 1977.
[14] RTeller, R.J.Brook and G.Petzow, *J.Hard Materials*, **2**, 79 (1991)
[15] S.K.Lee, D.Kim and C.K.Kim, *J.Mat.Sci.*, **29**, 4125 (1994)
[16] L.Wang, M.R.Wixom and L.T.Thompson, *J.Mat.Sci.*,**29**, 534 (1994)
[17] T.Cheng, J.Sun, *Scripta Metall.*,**30**, 247 (1994)
[18] D.E. Alman, N.Stoloff, *Int.J.Powder Metall.*,**27**, 29 (1991)
[19] A.U.Seybolt, *Trans.ASM* **59**, 860 (1966)
[20] S.C.Jha, R.Ray, *J.Mater.Sci.Lett.*7, 285 (1988)
[21] J.D.Whittenberger, R.K.Viswanadham, S.K.Mannan, B.Sprissler, *J.Mater.Sci.* **25**, 35 (1990)
[22] J.D.Whittenberger, S.Kumar, S.K.Mannan, R.K.Viswanadham, , *J. Mater.Sci.Lett. 9*, 326 (1990)
[23] S.K..Bhaumik, C.Divakar, L.Rangaraj, and A.K.Singh, *Mat.Sci.&Engg.* **A257**, 341 (1998)
[24] M.W.Barsoum and B.Houng,*J.Am.Ceram.Soc.*,**76**,1445 (1993)
[25] C.Divakar, S.K.Bhaumik, L.Rangaraj, S.Usha Devi and A.K.Singh, *Rev.High Pressure Sci.Technol.*,7, 1022 (1998)
[26] G.Zhang, Z.Jin, X.Yue, *J.Am.Ceram.Soc.* **78**,2831 (1995)
[27] T.Graziani, C.Melandri and A. Bellosi, *J.Hard Mater.* **4**, 29 (1993)
[28] W.Barsoum and T.El-Raghy, *J.Am.Ceram.Soc.*, **79**, 1953 (1996)
[29] T.Goto and T.Hirai, *Mater.Res.Bull.*, **22**, 1195 (1987)
[30] R.Pampuch, J.Lis, L.Stobierski, and M.Tymkiewicz, *J.Eur.Ceram.Soc.*, **5**, 283 (1989)
[31] F.Goesmann, R.Wenzel, and R. Schmidd-Fetzer, *J. Am.Ceram.Soc.*, **81**, 3025 (1998)